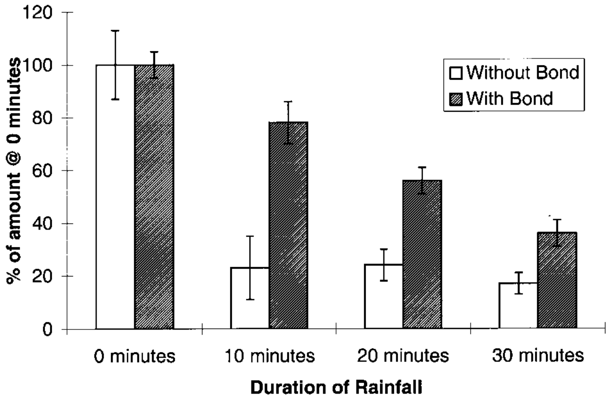

Figure 1. The effect of the adjuvant Bond on the mean amount of chlorpyrifos remaining on cabbage leaves after exposure to 10, 20 or 30 min rainfall. All data are shown as the amount remaining calculated as a percentage of the amount recorded on leaves that were not exposed to rainfall. Bar = SD.

the insecticide alone. Approximately 80% of the insecticide was washed off irrespective of the duration of rainfall. The increases in rainfastness with the other latex-based adjuvant ('Headland Guard') were also statistically significant for all treatment times. However, the improvement in deposit rainfastness with this adjuvant was by a constant factor of *c* 1.75. None of the other adjuvants assayed produced significant improvements in rainfastness for the rainfall treatment times used.

These results, which indicate that latex-based adjuvants can enhance rainfastness, are in broad agreement with other, similar studies that have been reported in the literature.[1,8–10] The main advantage with our approach, however, was that we were able to control exactly how much pesticide was applied to leaves and also to determine exactly how much had been removed. This meant that we were able to quantify the magnitude of the improvements in rainfastness that were realisable with the adjuvants tested. Therefore, our conclusion from these results is that latex-based adjuvants may be able to enhance dramatically the resistance of pesticides to wash-off. In the present work only two latex-based adjuvants were assayed and the work was carried out under laboratory conditions. For the future we intend to repeat these studies with other leaf surfaces and formulations and to undertake larger-scale field trials to assess whether improvements in rainfastness can translate into economic savings for growers via reductions in the number of pesticide applications that need to made to crops.

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Allium spp thiosulfinates as substitute fumigants for methyl bromide

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Abstract: Methyl bromide, the most widely used fumigant, is considered to be one of the major factors causing depletion of the ozone layer, and this is likely to lead to it being banned in the near future. *Allium* sulfur volatiles (thiosulfinates, R-S-SO-R′; R, R′ = Me, Pr, y Allul), known to be nematicides, have been evaluated as insecticides against insect pests in stored products, in comparison with their degradation compounds (disulfides) which have already been tested. Methyl and allyl thiosulfinates, with 24-h LD_{50} values of 0.02–0.25 mg litre^{-1}, were more active than disulfides against six test insects and were superior to methyl bromide; it is suggested that they could be used as alternatives to methyl bromide in stored product control.

Keywords: *Allium* spp, disulfides; fumigants; insects; methyl bromide; thiosulfinates

1 INTRODUCTION

Insect infestation, mainly by Coleoptera or Lepidoptera, causes major damage and loss during food storage, particularly in tropical areas. The control of such insect populations in stored products poses numerous problems. Mechanical or physical means are not in themselves sufficient. Only fumigants (acting in the gaseous state) are likely to diffuse through, and into, large masses of seeds. These fumigants are very effective on eggs and adults as well as on hidden stages, and leave very little or no residue.

However, chemical fumigants have similar drawbacks to synthetic pesticides used on cultivated crops

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in the field: their potential toxicity to humans and their potential impact on the environment.

Methyl bromide, the most widely used fumigant, is one of the major factors causing depletion of the ozone layer, and this is likely to lead to it being banned.[1] Therefore one must look at alternatives, including the use of natural fumigants, which may have less effect on the environment and so warrant further investigation.

The effects of plants, their extracts and plant-derived substances on stored-product insects have been investigated; they possess various physiological and behavioural activities. These include toxic, repellent and antifeedant effects.[2–5]

Extracts from *Allium* species, particularly garlic, *Allium sativum* L., are known to have both direct and inhibitory activity against a range of insect pests, including the eggs, larvae and adults of stored-products insects.

Allium spp show a characteristic, well-known resistance to many polyphagous insects and fungi, and are used in inter-cropping to protect, for example, carrots and potatoes from insect and other pests.[6,7] Also, when insects are reared on a diet containing *Allium* spp, they sequester sulfur volatiles which act as a deterrent to predators.[8,9] These observations suggested that *Allium* volatiles should be tested as fumigants.[10] The specific volatiles have been identified as thiosulfinates,[11] and this summary reports the evaluation of the toxicity of two compounds of this class in comparison with well-known fumigants such as methyl bromide, dibromoethane and dichloroethane, and with disulfides, the rearrangement compounds of the thiosulfinates, who toxicity has already been demonstrated.[10,12,13]

2 MATERIALS AND METHODS

2.1 Insects

he insects used were one-week-old adults reared by standard procedures: *Sitophilus orizae* L, *S granarius* L, *Ephestia kuehniella* Zell and *Plodia interpunctella* Hübn, were maintained at a photoperiod of L:D 16:8h at a synchronous thermoperiod 25°–16°C and RH 65–75%. *S. orizae* was reared on wheat, *S. Granarius* on maize, *E. kuehniella* on flour, and *P. interpunctella* on crushed maize with glycerol.

Callosobruchus maculatus F. and *Bruchidius atrolineatus* (Pic) were reared on cowpea (*Vigna unguiculata* Auct.) with a photoperiod L:D 16:8h at a constant 30°C and RH 70–80%.

2.2 Chemicals

Methyl bromide, dichloroethane, dibromoethane, dimethyl disulfide and dially disulfide were obtained from Aldrich. Diallylthiosulfinate and dimethylthiosulfinate were synthesize as previously described.[14]

2.3 Fumigation procedure

The fumigation chambers were desiccators (12 litre capacity) sealed with silicone vacuum grease and equipped with a glass stopper. The compounds, liquid at room temperature, were deposited with a syringe on Whatman filter paper (No. 1; 2 × 5 cm) placed in the bottom of the desiccator. For methyl bromide, the fumigant was refrigerated and withdrawn with a gas-tight refrigerated syringe from a pressurized container. The insects were then rapidly introduced into the desiccator by a funnel placed in the stopper cavity.

Various time-series of exposures were conducted for each of the six test species to obtain a dose–toxicity curve from which LD_{50} (μl fumigant litre^{-1} air) was estimated. Each fumigration trial consistent of simultaneously exposing a group of 50 insects (25 males, 25 females) to the fumigant at four concentration levels and to a control in pure air at room temperature for 24h. The desiccator was then opened and the number of dead insects was determined after exposure to fresh air (24h) because some insects can survive although appearing to be dead immediately after exposure to fumigant.

Table 1. Activities of methyl and allyl thiosulfinates against stored-product insect pests, compared with those of some commercially used fungicides

Insects	*Fumigants* LD_{50} (*mg litre*$^{-1}$)[a]						
	Methyl thiosulfinate	*Allyl thiosulfinate*	*Methyl disulfide*	*Allyl disulfide*	*Dibromo-ethane*	*Dichloro-ethane*	*Methyl-bromide*
Ephestia kuehniella	0.04	0.02	0.17	0.02	0.85		
Plodia interpunctella	0.02						
Bruchidius atrolineatus	0.15	0.18	0.23	0.60			
Sitophilus granarius	0.14						
Sitophilus oryzae	0.19		1.23		2.66	4.13	1.05
Calosobruchus maculatus	0.25	0.16	1.06	0.58	0.72	3.71	

[a] 24 h exposure.

3 RESULTS

The LD_{50} values (24 h) of dimethyl- and di-allyl-thiosufinate were comparable, varying from 0.02 mg litre^{-1} against *P. interpunctella* to 0.25 mg litre^{-1} against *C. maculatus*, although those for thiosulfinates were generally lower than those for disulfides.

In comparison, 24-h LD_{50} values for some classical fumigants, tested in the same apparatus against three of the test species, were higher than those for the thiosulfinate compounds: they varied from 0.72 mg litre^{-1} for dibromoethane/*C. maculatus* to 4.13 mg litre^{-1} for dichloroethane/*S. oryzae* and were *c* 3–40 times higher than those for thiosulfinates. In all cases, Lepidoptera were more sensitive to the compounds than Coleoptera.

4 CONCLUSION

In addition to the known nematicidal activity of thiosulfinates,[15] the results indicate their potential in fumigation of stored products. They appear in fumigation of stored products. They appear to be possible substitutes for methyl bromide. These compounds need to be fully explored in terms of pungency and stability, as the lability of these active substances seem to exist only in the liquid state.[16]

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Synthesis and insecticidal activity of nitroguanidine derivatives

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Abstract: Nitroguanidine derivatives with thiazol-5-ylmethyl moieties were prepared and their insecticidal activities against homopterous pests were tested. New synthetic routes for 2-chloro-5-chloromethylthiazole from 2,3-dichloro-1-propene and for substituted nitroguanidines from *S*-methyl-*N*-nitroisothiourea were established. Biological evaluation led to a novel insecticide (*E*)-1-(2-chlorothiazol-5-ylmethyl)-3-methyl-2-nitroguanidine (TI-435) which has a broad activity spectrum and is under development.

Keywords: neonicotinoid; nitroguanidine; insecticidal activity; structure–activity relationship; TI-435

1 INTRODUCTION

So-called neonicotinoids are establishing themselves as a new class of insecticide.[1,2] The first successful member of this family was imidacloprid,[3] developed by Nihon Bayer Agrochem KK, Japan. Takeda Chemical Industries, Ltd has already commercialised the acyclic neonicotinoid, nitenpyram,[4] which is highly active against homopterous and thysanopterous pests.

This summary describes a continuation of the study on neonicotinoids which showed that acyclic nitroguanidine analogs with a thiazol-5-ylmethyl group have also good activity (Fig. 1).

2 METHODS

2.1 Synthesis

The synthetic routes for the thiazol-5-ylmethyl moieties are described in Fig. 2. 2-Amino-5-methyl-

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